Mechanical Adaptivity as a Process: Implications to New Materials and Material System Design

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Functional Materials Division
Materials and Manufacturing Directorate

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AFRL Materials & Manufacturing Directorate

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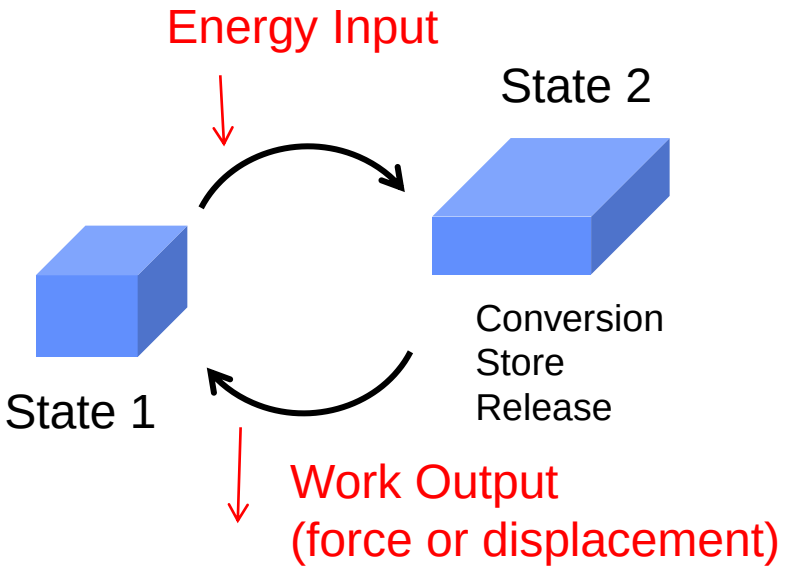
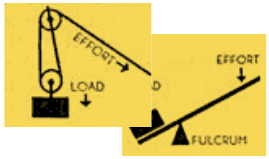
What is Mechanical Adaptivity?

Energy Transduction Process Producing Force or Motion

- Conversion of Energy to Work
- Store Mechanical Energy and Release
- Combination



Mechanical Design Analogy:



Simple Machines → Mechanical Design → Advanced Functions

Building Blocks

Materials that display:
1) Autonomous behavior
2) Respond to multiple stimuli
3) 3D, rapid actuation

Knowledge & Predictive Models

Accurate math models enable predictive design

Fabrication of Architecture:
Greater than sum of the parts

Architecture design with responsive materials leading to enhanced functionality

Program Status

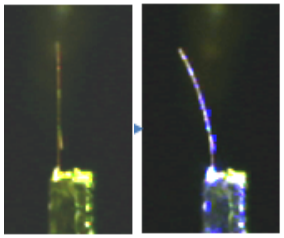
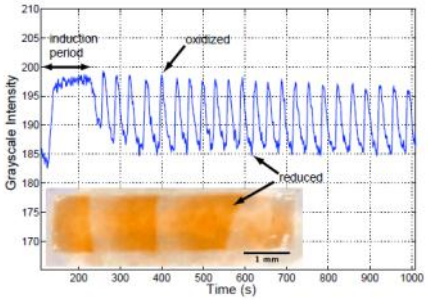
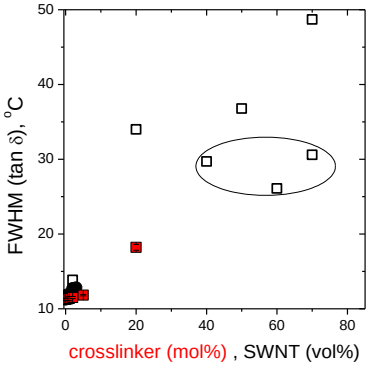
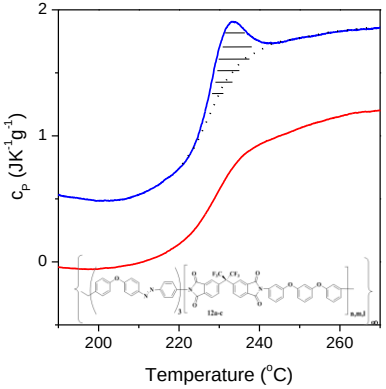
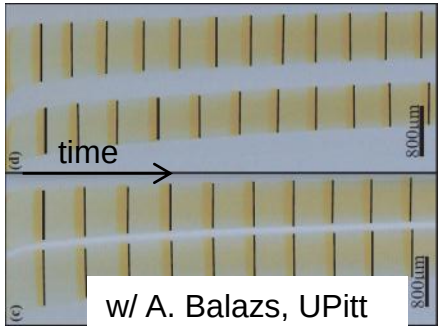
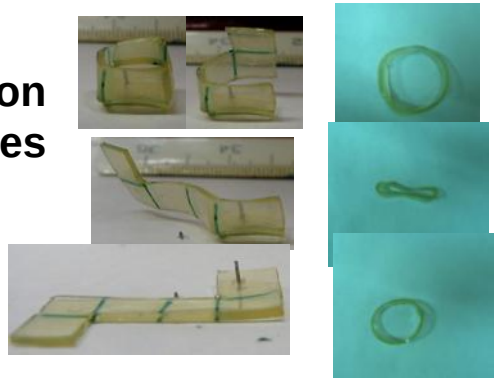
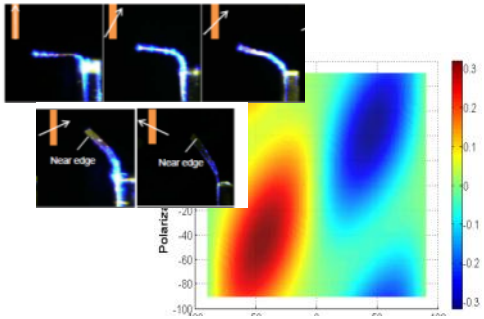
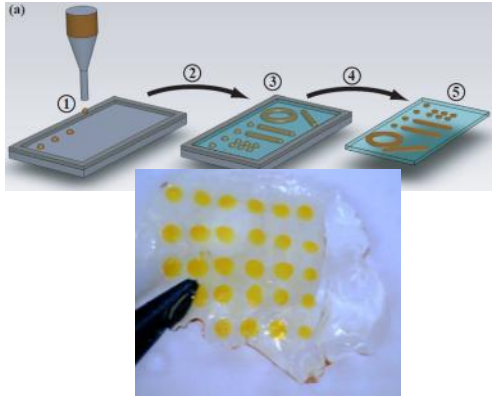
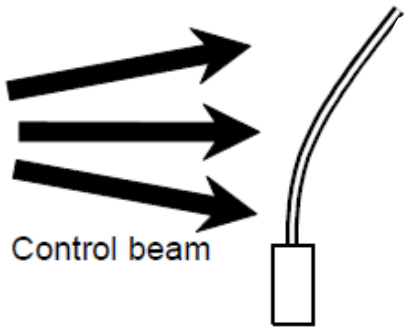
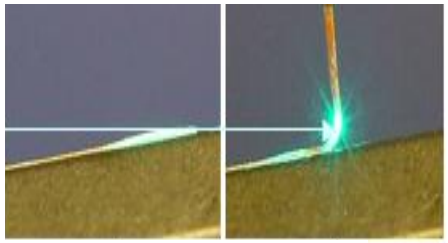
	HT Thermal Shape Memory	PhotoChem-Mechanical	Autonomic Chemo-Mechanical
Building Blocks	 w/ L-S Tan, AFRL	 w/ T. White & L-S Tan, AFRL	
Predictive Models			 w/ A. Balazs, UPitt M. Smith, Hope C.
Fabrication of Devices		 w/ T.White & M. Smith, Hope C.	

Photo Mechanical: Aerospace Applications



Beam Steering



Ar+ blocked I = 4 mW/cm^2

Tabiryan et al BEAM Unpublished. Bunning, Optics Express, 2009. Tabiryan & White Optic Express 2010

h_n —energy→ heat, charge, photochem

transduction

↓ amplification ↓

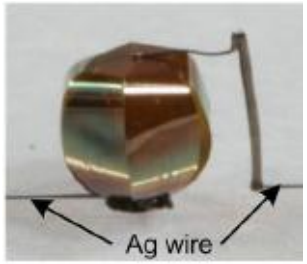
phase change, concentration

↓ summation ↓

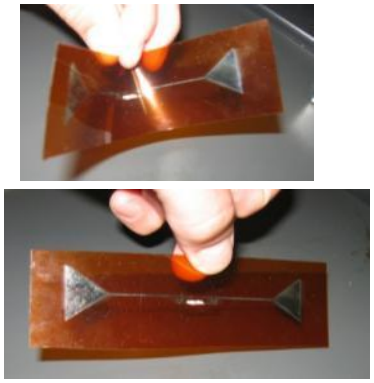
gradient

Tuning Receivers and Packages

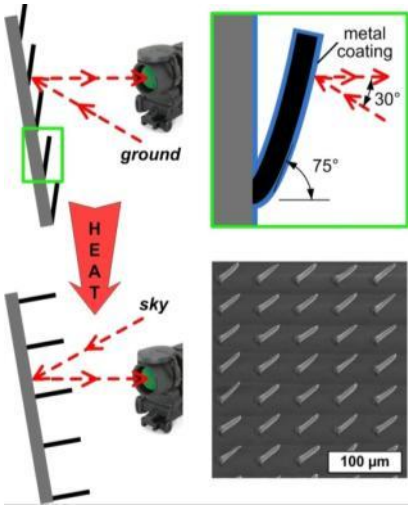
3D Photovoltaics



Nuzzo et al., *PNAS* **106** 2009



Vaia et al 2012

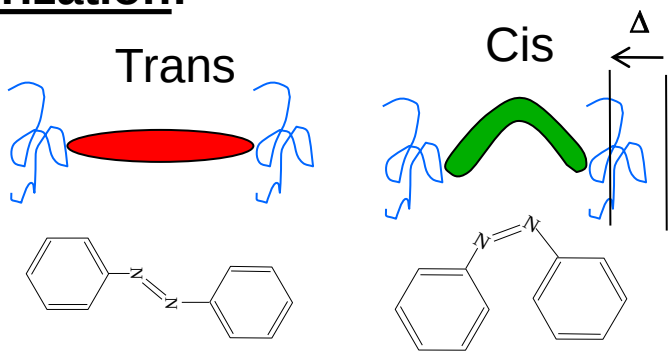


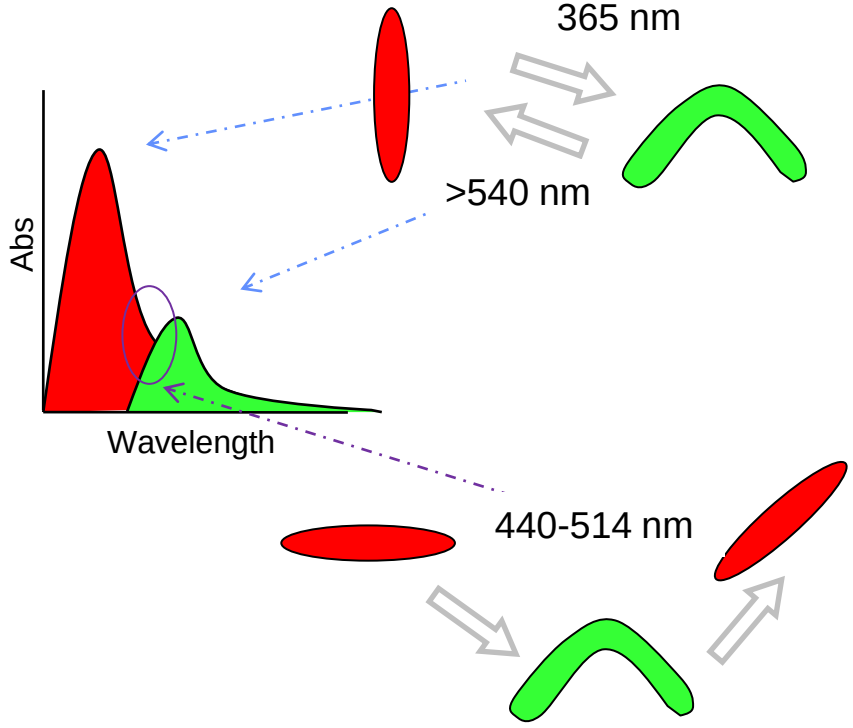
John Hart, Davor Copic, University of Michigan

Remote & Focused Trigger

PhotoChem-Mechanical Response: Azo

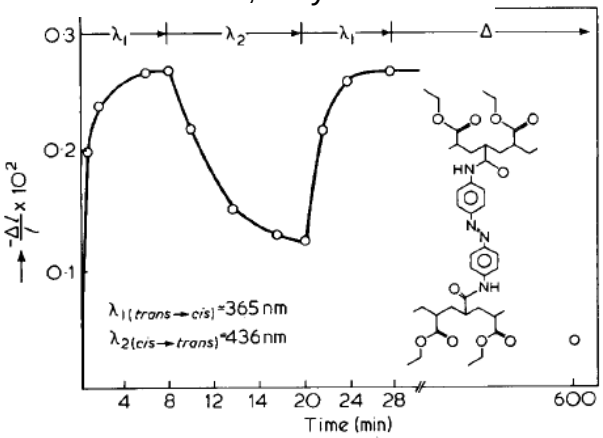
Isomerization:

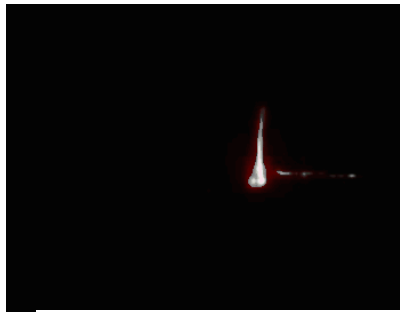




"Glassy" Networks: Azo & LC

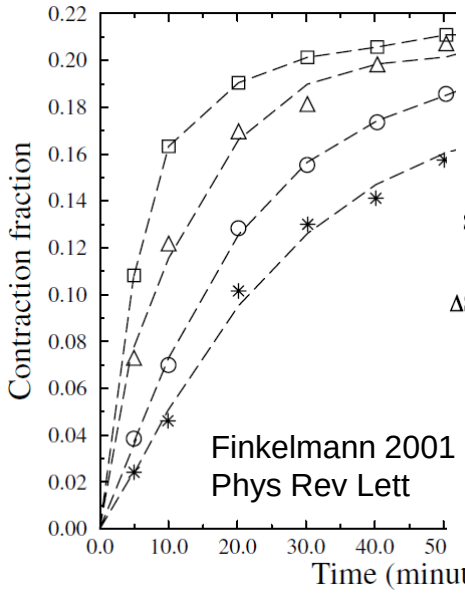
Eisenbach, Polymer 1980



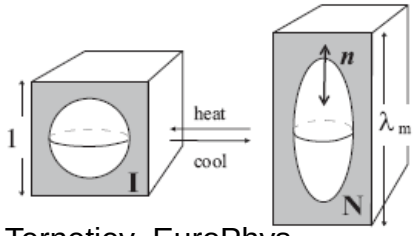


White, et al AFRL 2008

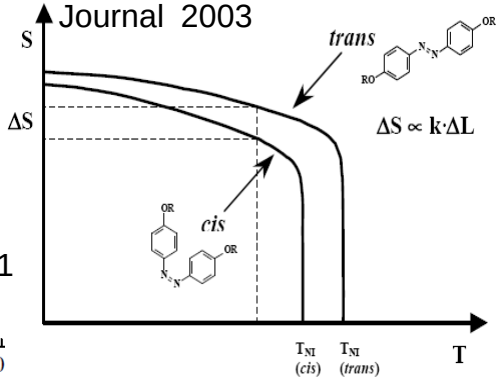
Elastomers: LC-Azo



Finkelmann 2001
Phys Rev Lett



Ternetjev EuroPhys Journal 2003

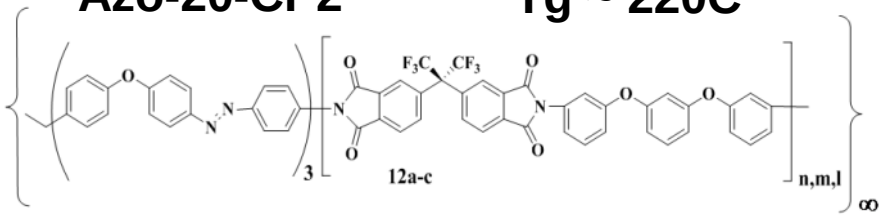


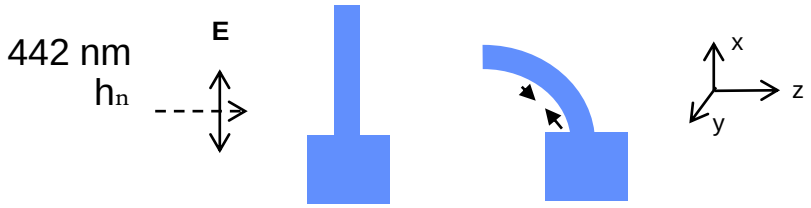
Tuning Photo-Mechanical Response with Process History

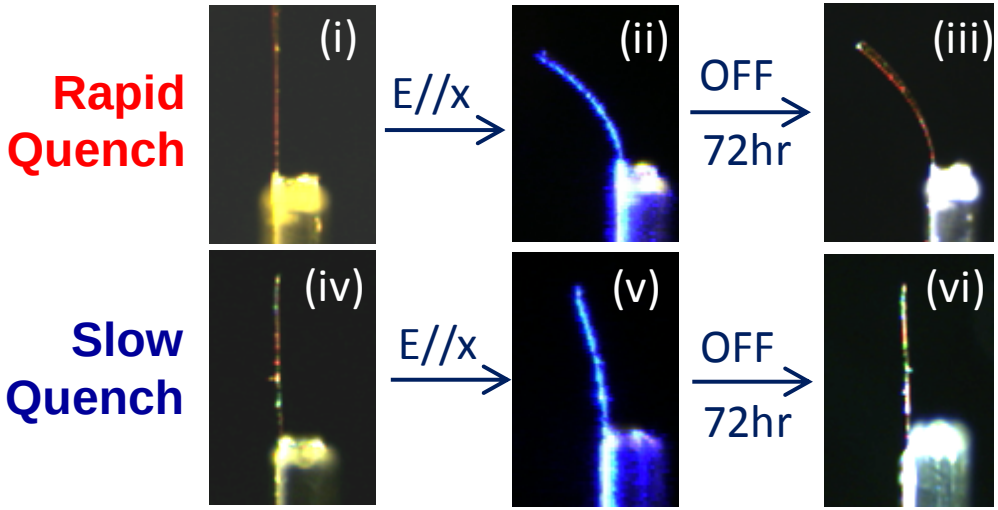
Photo-Plastic (Photo Set, Photo Hardening)
Remove light, retain shape

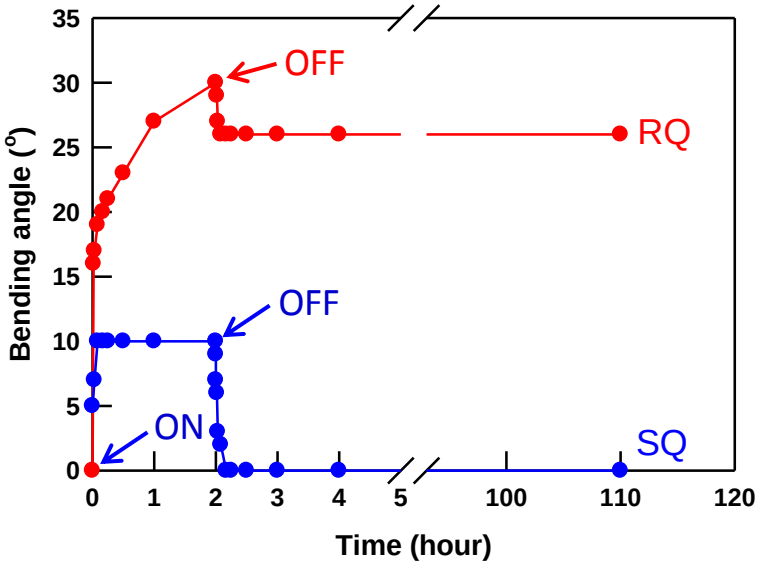
Photo-Elastic (Photo Recovery)
Remove light, recovery original shape

Azo-20-CP2 **Tg ~ 220C**



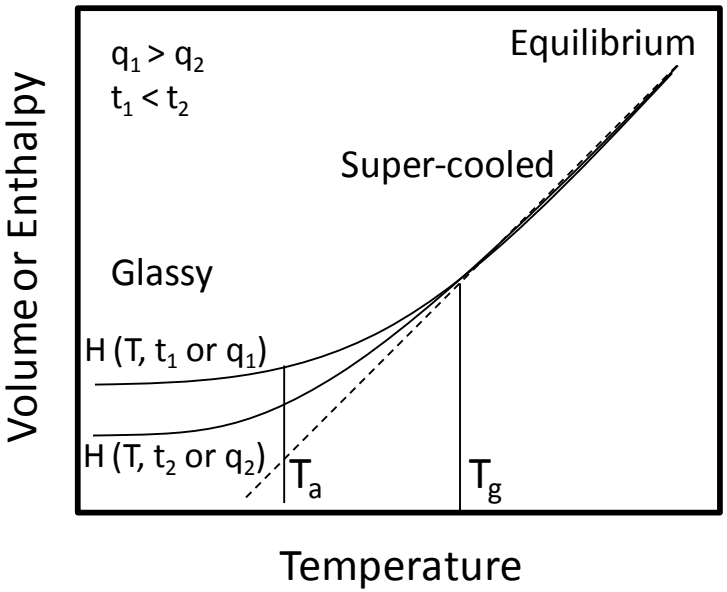


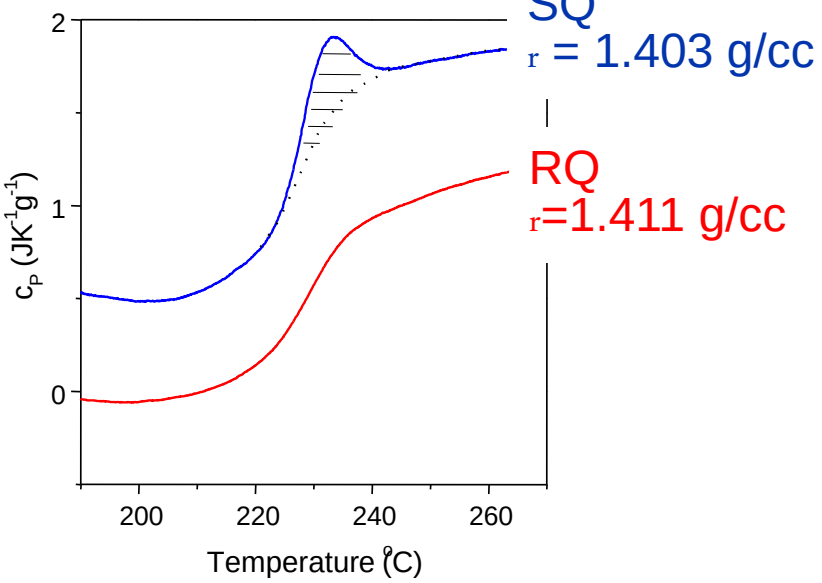


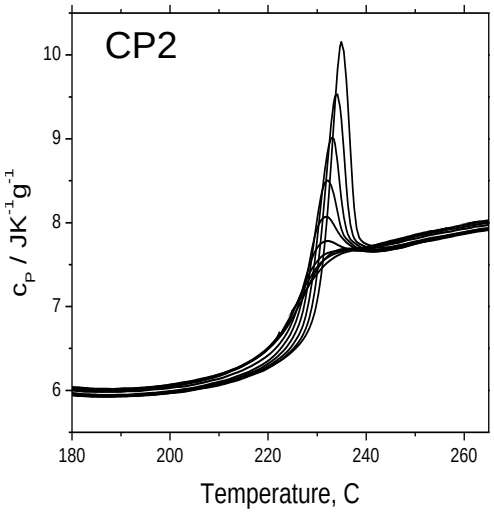


Vaia, White, Tan et al. submitted 2012

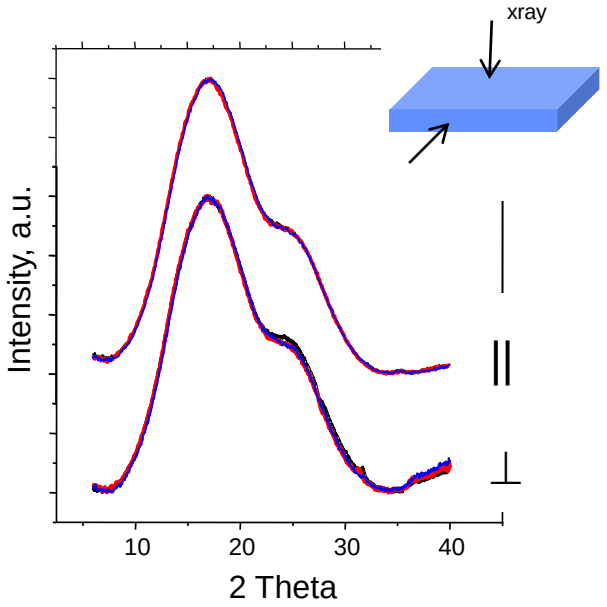
Glass Structure







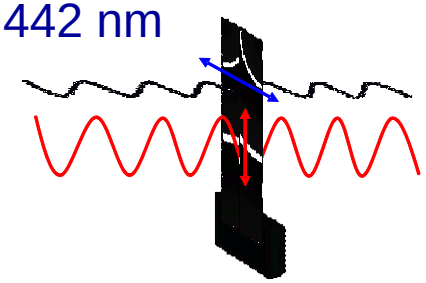
	Tg [K]	Δh [kJ/ mol]	β	M
CP2	498	975	0.84	108
azo-5-CP2	500	980	0.71	110
azo-20-CP2	505	1500	0.46	150



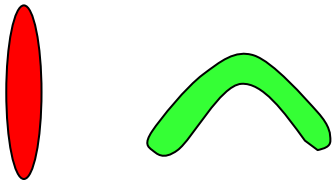
Vaia, White, Tan et al. submitted 2012

Molecular Dynamics

442 nm

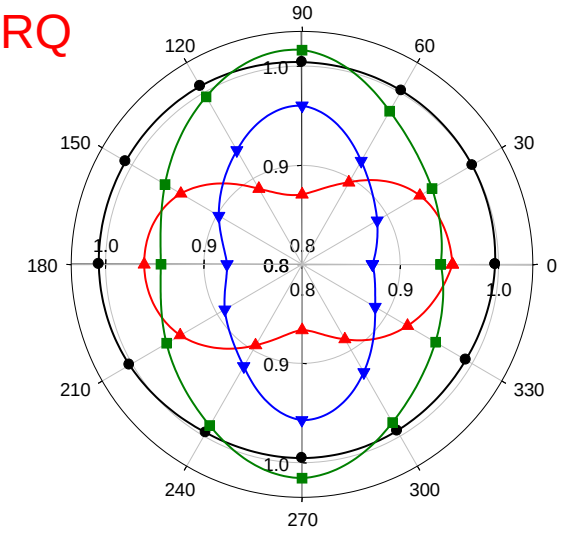


***Trans*-isomer** ***Cis*-isomer**

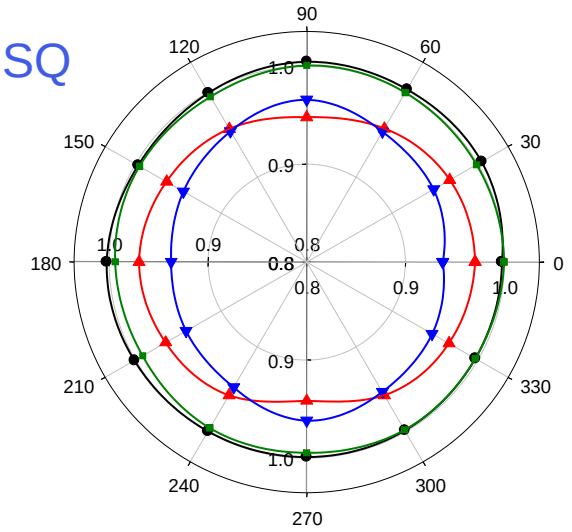


Relative Abs: Trans Isomer (355 nm)

RQ



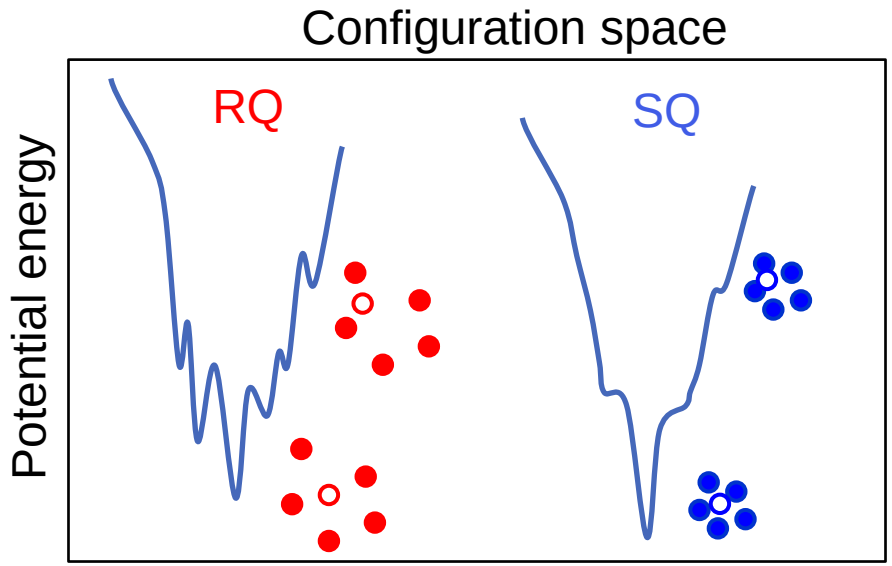
SQ

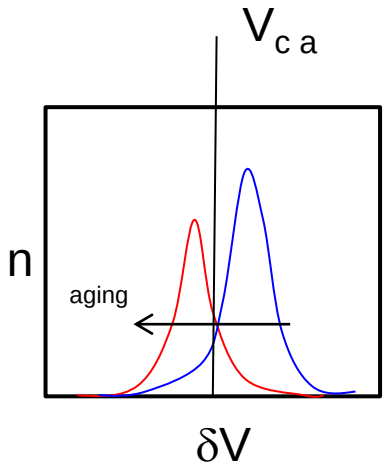


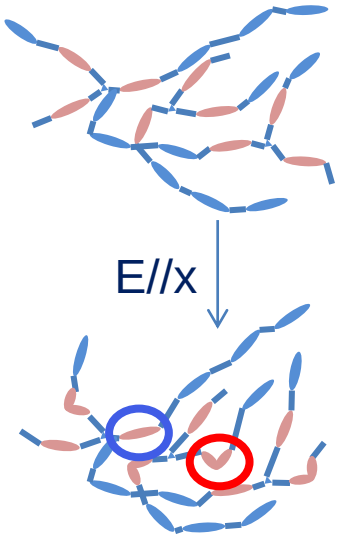
- Isotropic trans distribution
- 442 illumination:
  - trans rotation + 3-5 % cis
  - RQ > SQ
  - Reversible & $\perp$ E
- Dark state:
  - RQ partial recovery consistent with cis, trans enhancement
  - SQ initial state recovery

Vaia, White, Tan et al. submitted 2012

Glass Energy Landscape for Photo Chemical to Mechanical Transduction

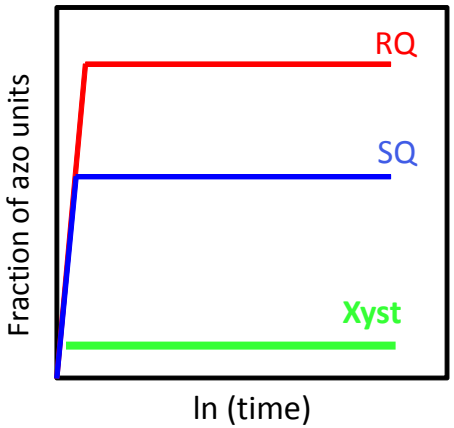






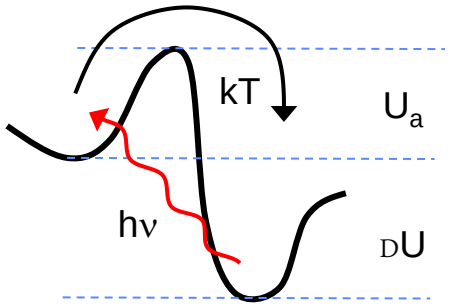
Photon to Isomerization

$\epsilon \sim s\, f_{isom}$



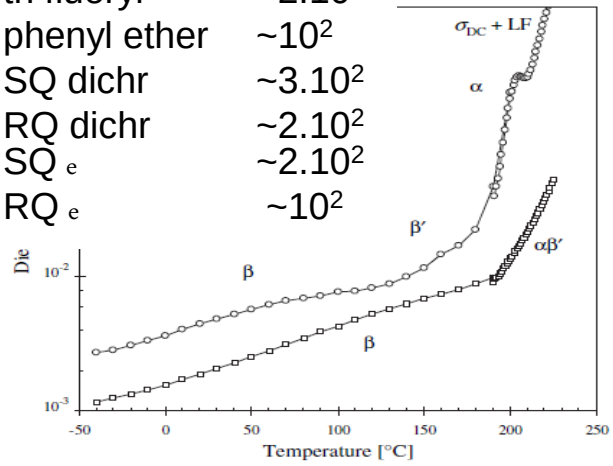
Internal Energy Storage & Recovery

$$\frac{\epsilon_{plastic}}{\epsilon_{elastic}} \sim f\left(\frac{U_a}{kT}\right)$$



Recovery Rates

	$t_{1,RT}$
tri fluoryl	~2.10^7
phenyl ether	~10^2
SQ dichr	~3.10^2
RQ dichr	~2.10^2
SQ $_e$	~2.10^2
RQ $_e$	~10^2



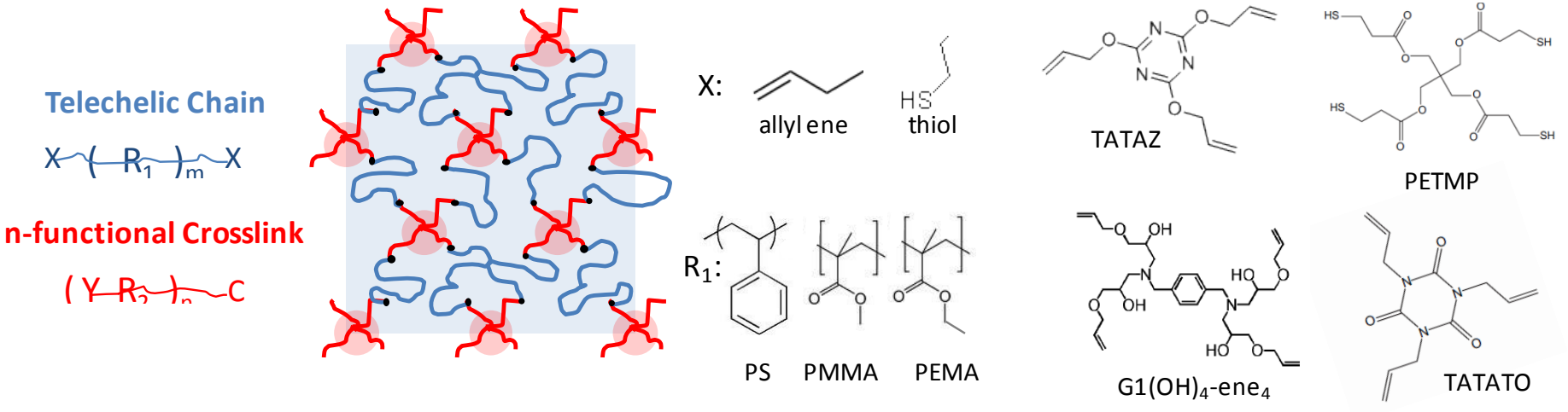
Implications & Next Steps

Distribution of local "activation volume" controls first step for molecular to macroscopic transduction

- Molecular structure ***and*** process history
- Fraction of successful photon-to-isomerization events
- Fraction of trapped events
- Rate of recovery of events

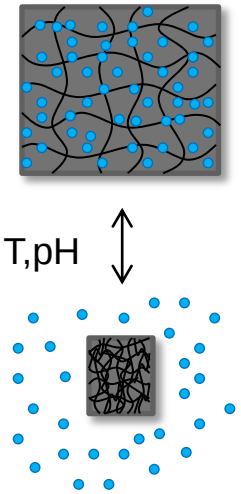
Material System Architecture to Optimize Speed and Efficiency

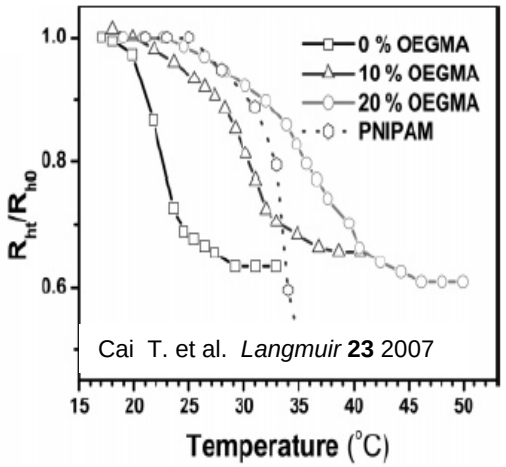
- $_{D}U \sim {}_{r}$ (isomerization) I (**x**) E (**x**)
- Local anisotropy – LCs v. semi-rigid v. flexible chains
- Network structure, secondary relaxations, local of "hinge"
- Photochemistry: rotation v. cis formation



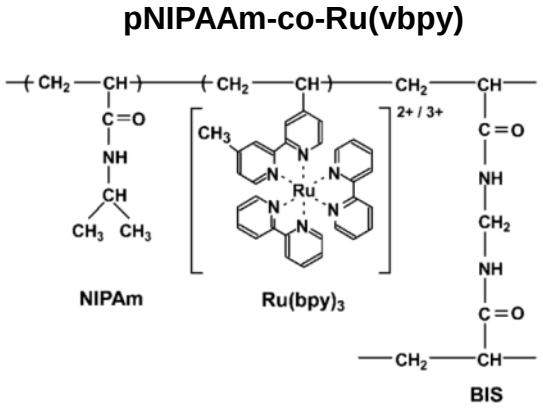
Autonomic Chem-Mechanical Systems: Responsive Hydrogels & Chemical Oscillators

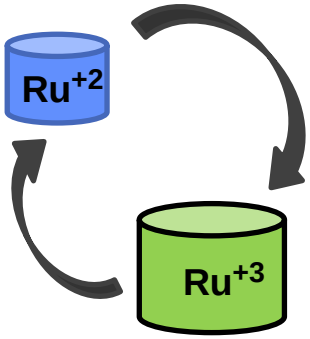
Responsive Hydro-gels



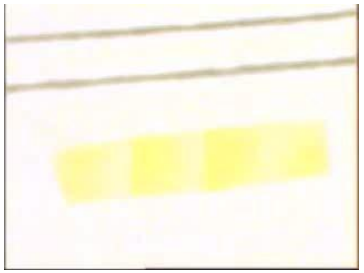


Autonomic Chem-Mechanical Systems

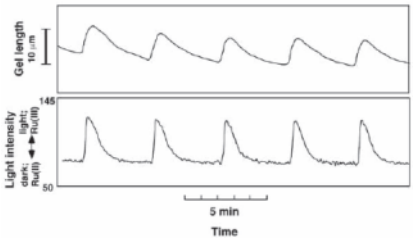




R. Yoshida



M. Smith

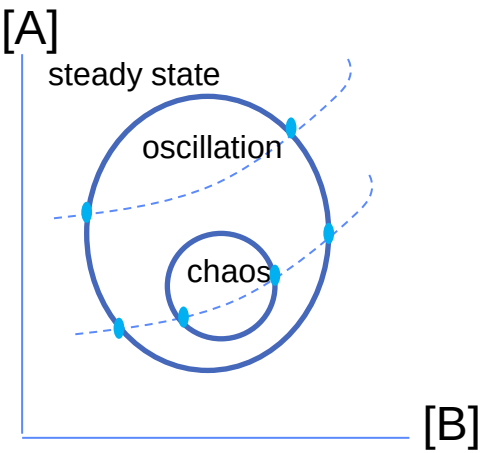


Chemical Oscillator

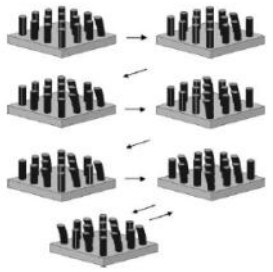
Stirred BZ reaction

BZ Reaction

$M_{red} \longleftrightarrow M_{ox}$



Maeda et al. Int. J. Mol. Sci. 2010



Tabata et al. Sensor Actuat. A. 2002

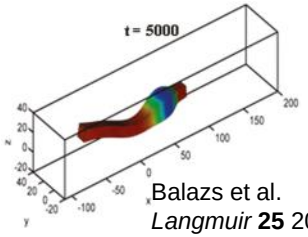
Heterogeneous Chem-Mechanical Design

Heterogeneous Autonomic Systems = Composite w/ Active & Inactive Regions

- Homogenous Autonomic Gel = Strain Generator Unit
- Amplify Motion through mechanical architecture
- Coupled feedback through
  - Chemical Concentration gradients
  - Mechanical-Chem interactions

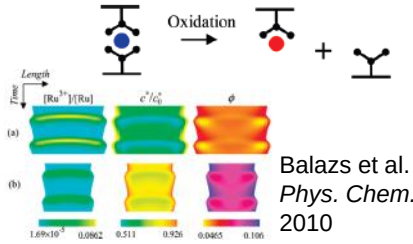
Potential routes for control

Photo Directed Motion

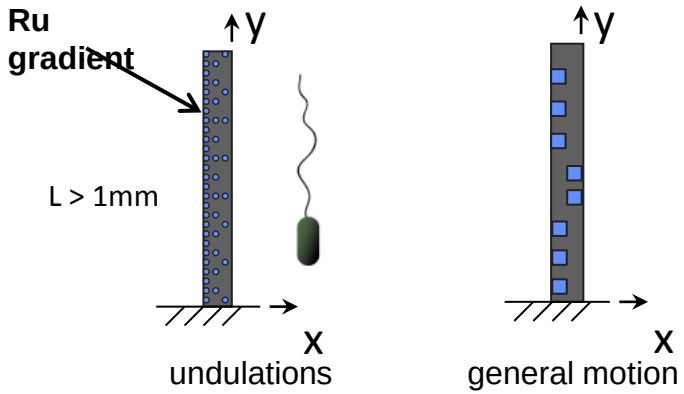


Balazs et al. *Langmuir* **25** 2009

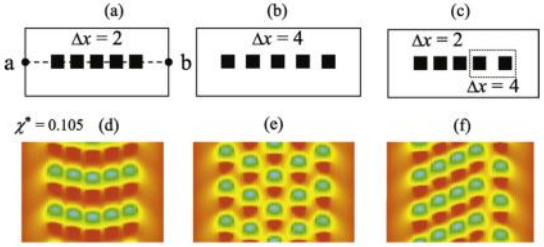
Oscillating Elasticity



Balazs et al. *J. Phys. Chem. B* **114** 2010



Coupled Oscillator patches:
2D patterning allows for phase control of osc



Balazs et al. *Prog. Polym. Sci.* **35** 2010

Westbrook and Qi. *J. Intell. Mater. Sys. Struct.* **19** 2008

Patterning Structure and Active Regions

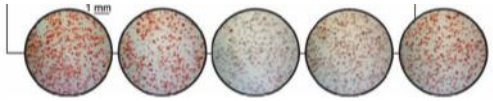
Structured Heterogeneous Gels

Physical Composite

Monolithic Composite

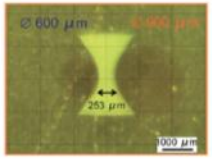
Assembly - arrange premade, discrete homogenous units

- Adv: Flexibility in design
- Dis: minimal mechanical coupling, weak structures, very slow, poor reproducibility

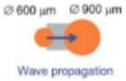


Showalter et al. *Science* **323** 2009
Steinbock et al. *Science, **269*** 1995

Steinbock et al. *J. Phys. Chem.* ***100*** 1996



Yashin, *et al J.Mater.Chem*, 2012



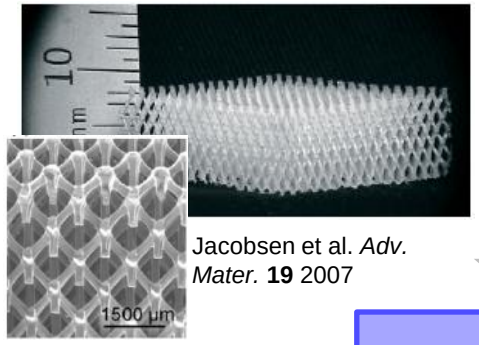
Van Vliet, *Adv. Func. Mater*, 2012

Photopolym - in plane patterning of monomer mixture

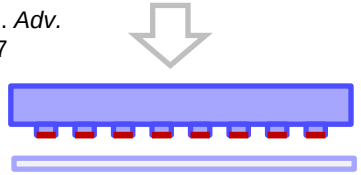
- Adv: Precision control to micron scale
- Dis: catalyst photo sensitive, limited flexibility (new form for new app)

Postfunctionalization - separate form from pattern (add catalyst & x-linking later)

- Adv: Flexible for 2D (on-demand stamping), Pattern 3D structures
- Dis: Completeness of reaction, profiles dependent on diffusion



Jacobsen et al. *Adv. Mater.* **19** 2007



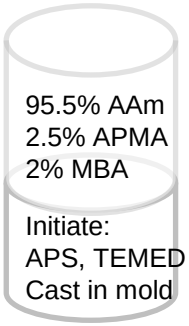
Vaia, Smith, SPIE 2012

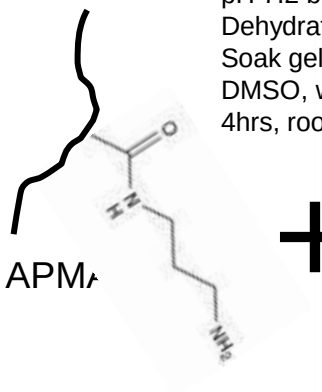
Additive Manufacturing – printing 3D (involve postfunctionalization, thermo-gelling, etc..)

- Adv: 3D structures (additive manufacturing)
- Dis: Resolution limits, processing variables

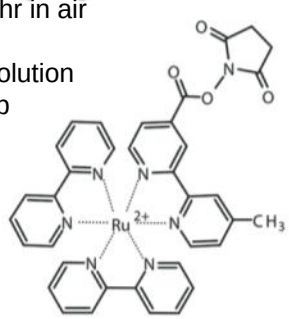
Vaia, et al 2012

Postfunctionalization: Polyacrylamide



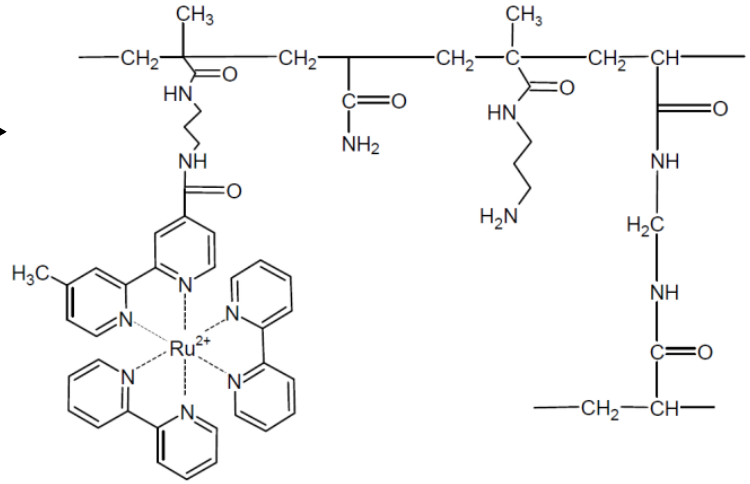


pH 7.2 buffer
Dehydrate for 1hr in air
Soak gel in Ru,
DMSO, water solution
4hrs, room temp



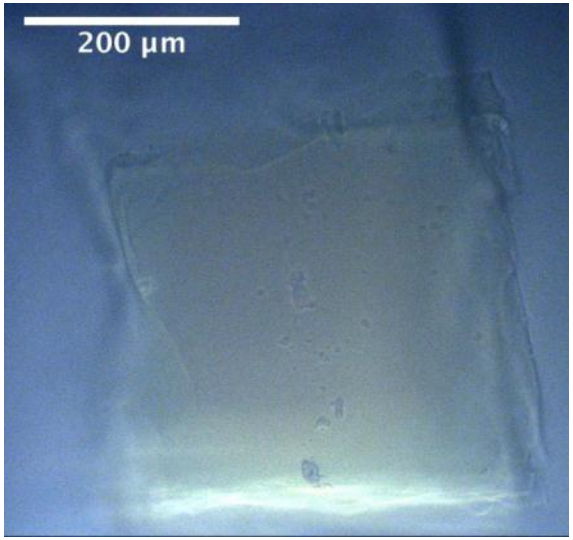
Polymer ***or***
Swollen Network

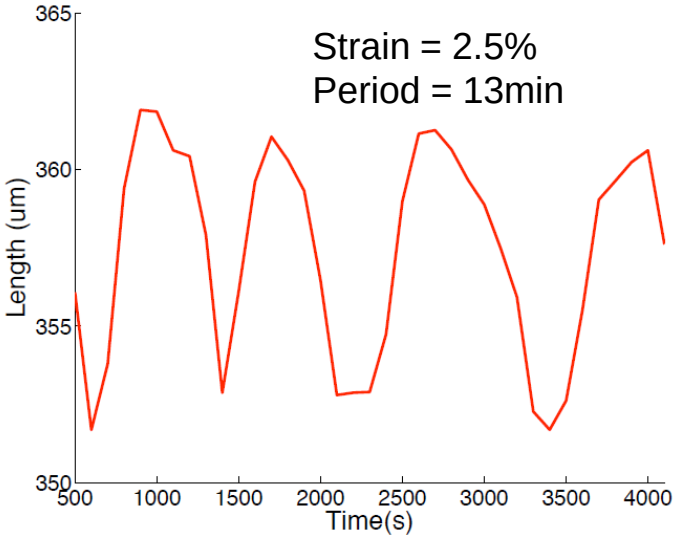
poly(AAm-co-AMPA-co-Ru)



Immerse in BZ Soln

0.08M Sodium Bromate
0.04M Malonic Acid
0.7M Nitric Acid



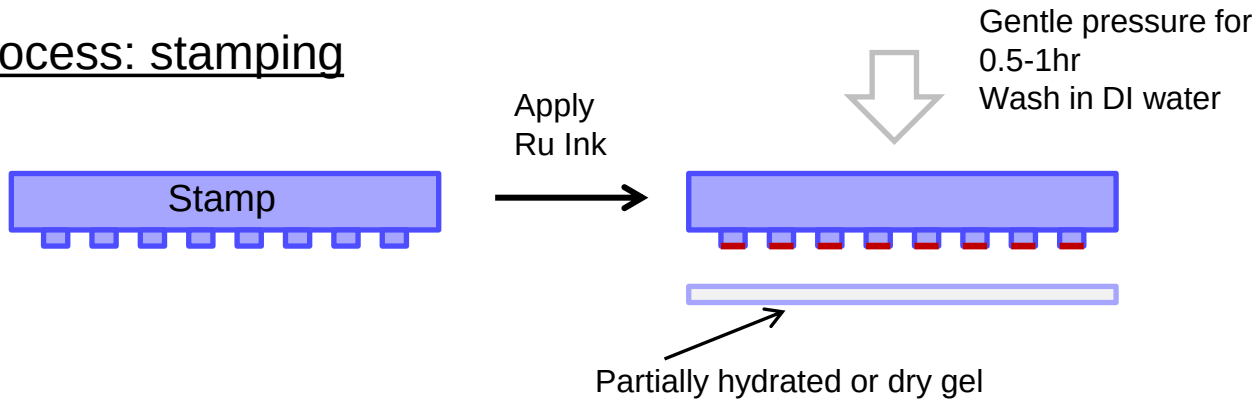


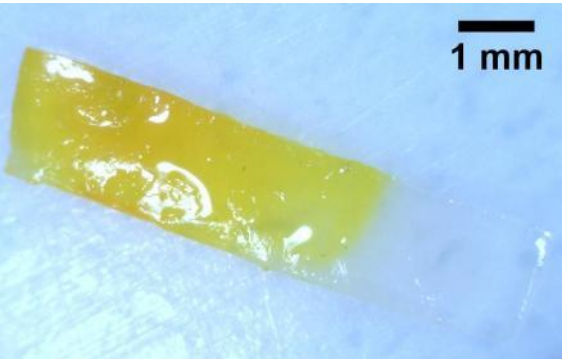
Literature: Typical strains = 2-20%

Conner, Smith, Vaia et al. submitted 2012

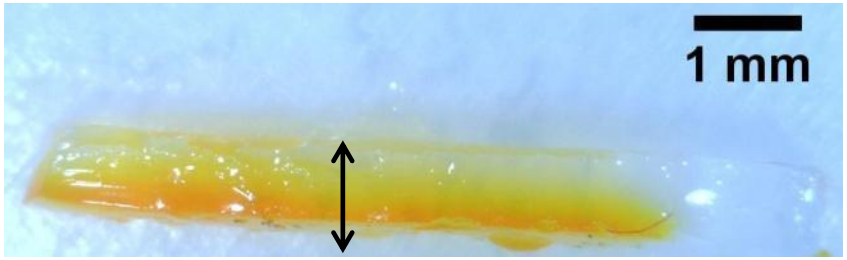
Patterning poly(AAm-co-APMA)

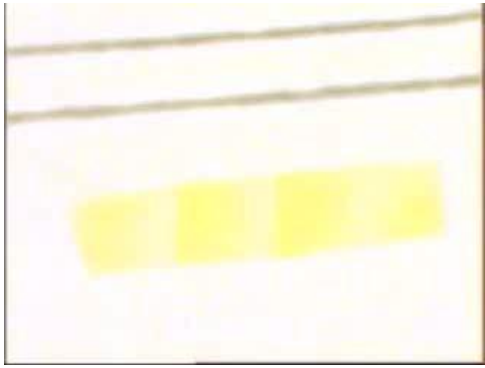
Process: stamping

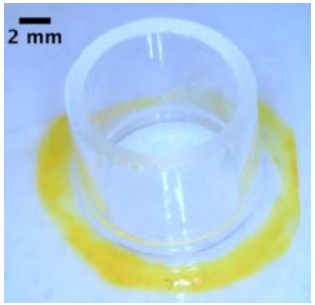




Gel Cross Section - Ru Gradient







Large Circular Pattern

Chemical wave periods: 4-10min

Current Challenge: Improve control over diffusion and pattern size

Conner, Smith, Vaia et al. submitted 2012

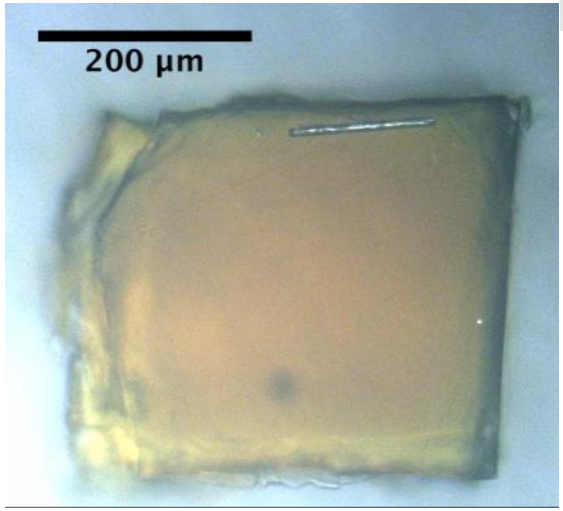
BZ-Gelatin for Thermogelling

Thermogel

- physically crosslinked (H-bonds, xystals)
- melts above a critical temperature

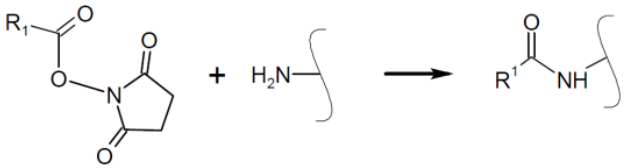
Ru conc: 0.04-0.05%

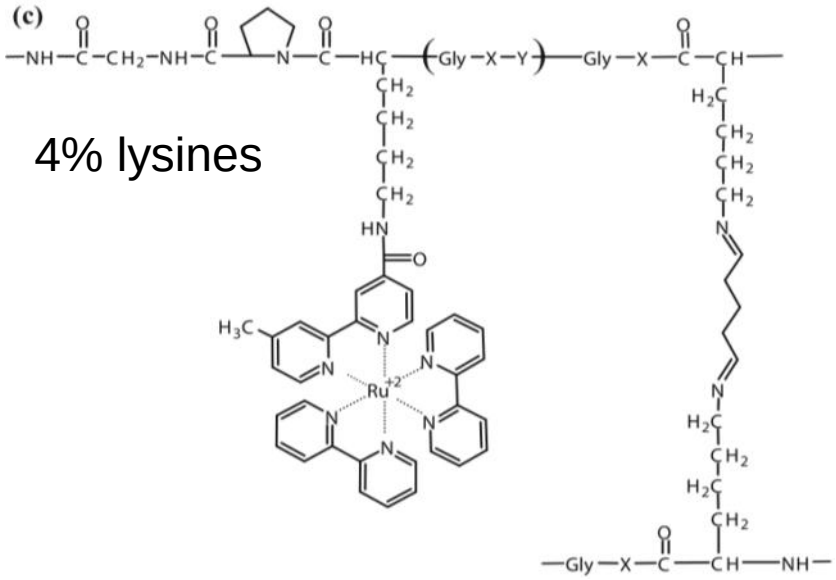
Chemical wave periods (>1mm): 2-6min



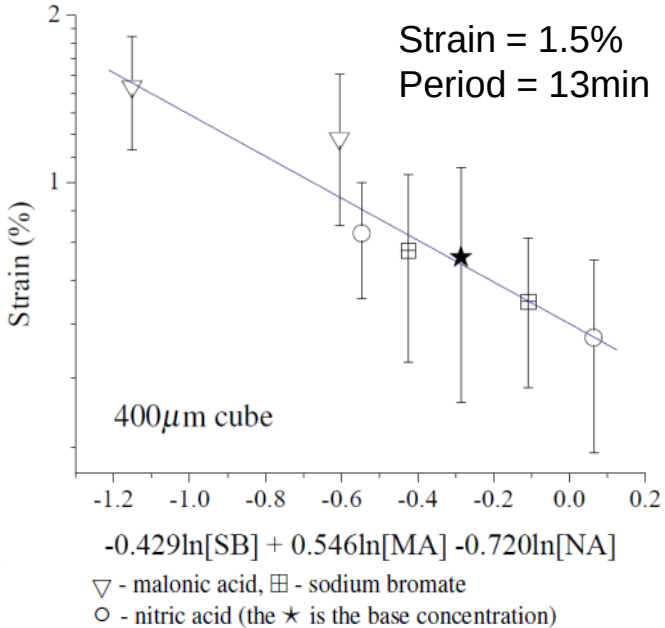
0.08M Na Bromate
0.04M Malonic Acid
0.7M Nitric Acid

Type A BZ Gelatin

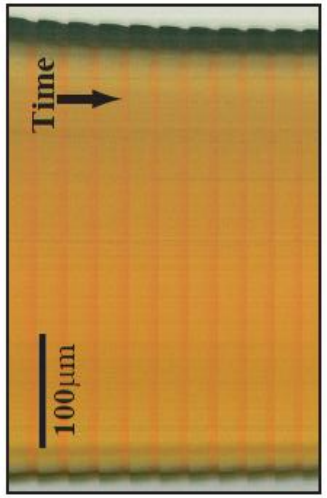




4% lysines

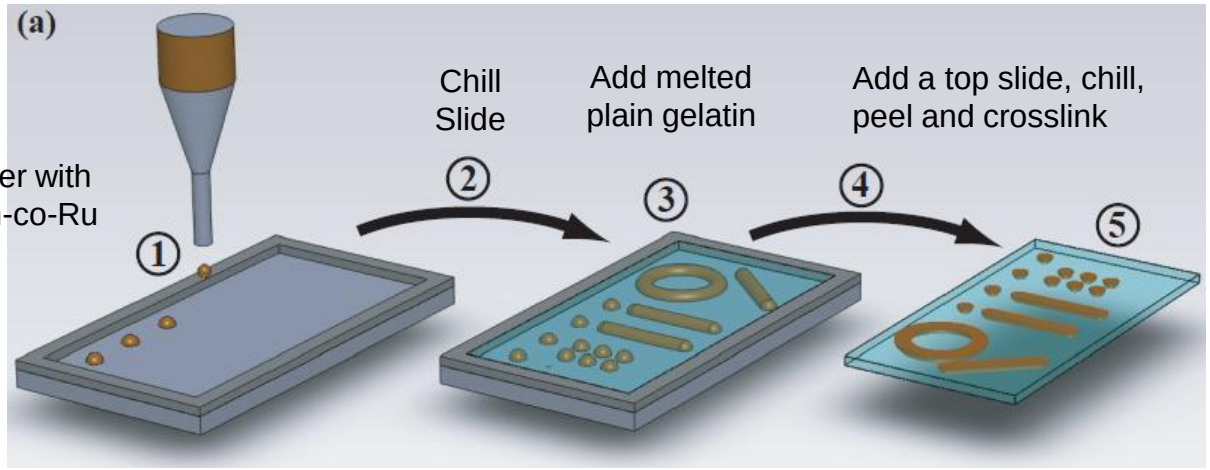


Strain = 1.5%
Period = 13min

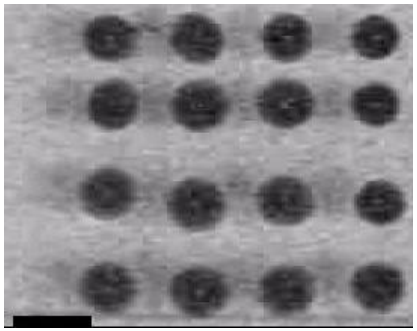


Smith, Vaia et al. Chem Mater 2012

Additive Mfg: Patterned Gelatin



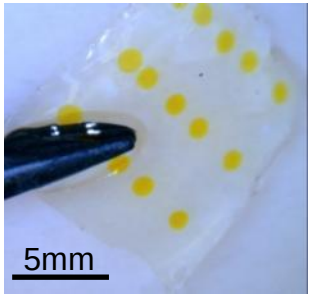
Array of Freestanding Dots in BZ Solution

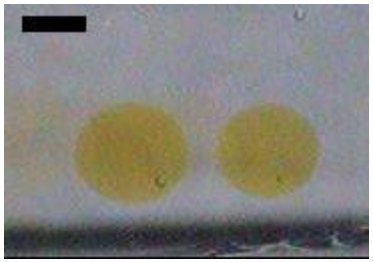


0.08M Sodium Bromate
0.06M Malonic Acid
0.7M Nitric Acid

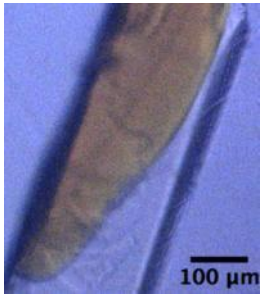
Smith, Vaia et al. submitted 2012

Heterogeneous Gel

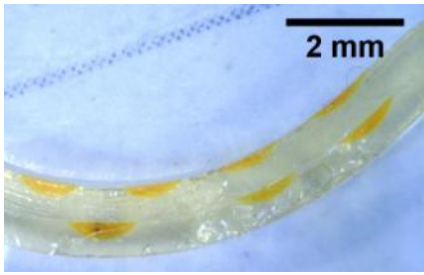




Cross Section

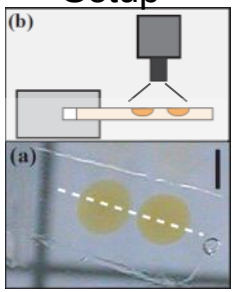


3D Pattern



Adjacent Patches: Effects of Spacing

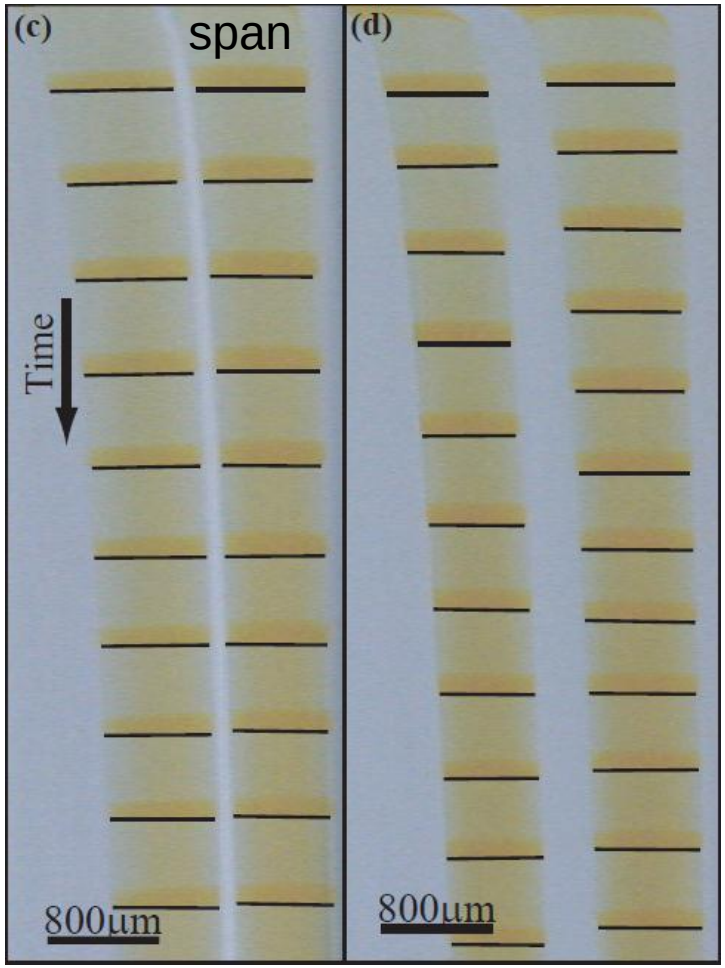
Setup



Coupled Osc.

0.08M Sodium Bromate
0.02M Malonic Acid
0.7M Nitric Acid

~6 hr time span



Summary

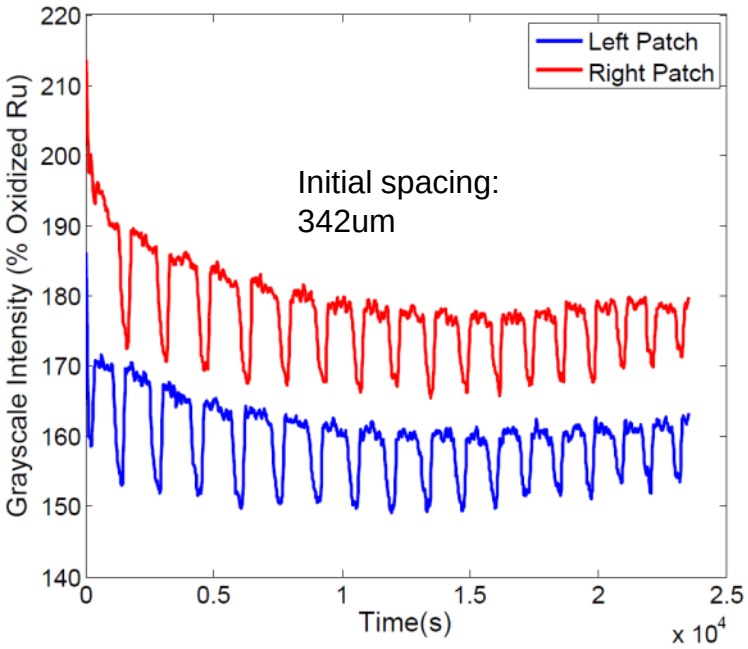
1 patch
- Period = 2039 +/- 251

2 close patches
- Inner spacing = 117 +/- 13um
- Period = 1613 +/- 244
- Ave diff in period: 0-34s

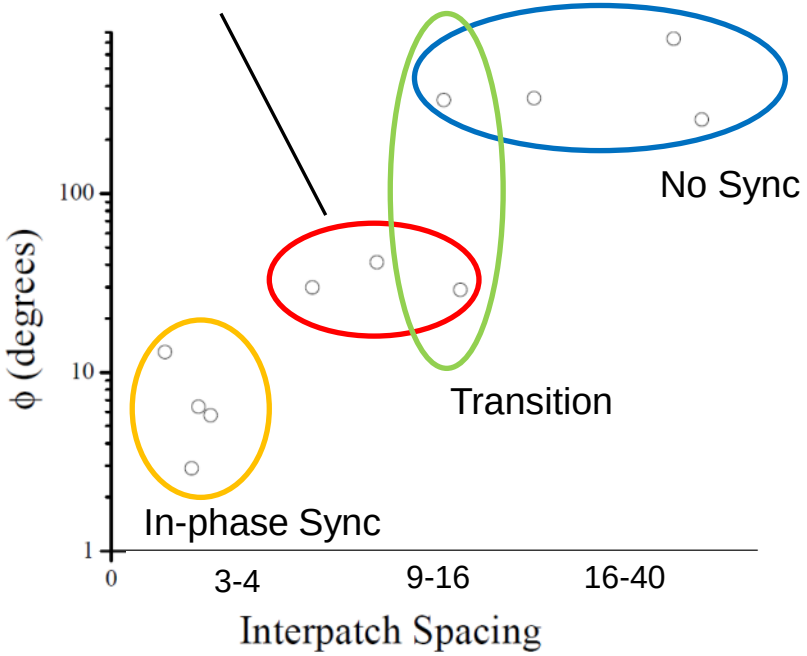
2 far patches
- Inner spacing = 628 +/- 160um
- Short (clamp) = 1547 +/- 332
- Long (free end) = 1962 +/- 429
- Ave diff in period: 120-751s

Smith, Vaia et al. submitted 2012

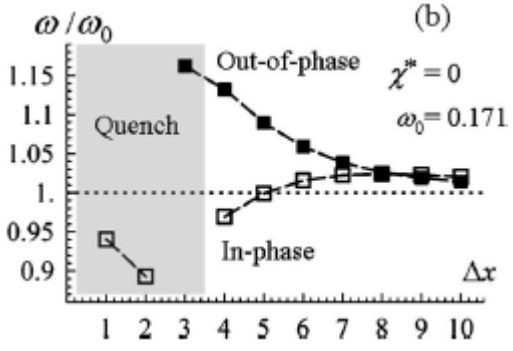
Synchrony Comparison to Simulation



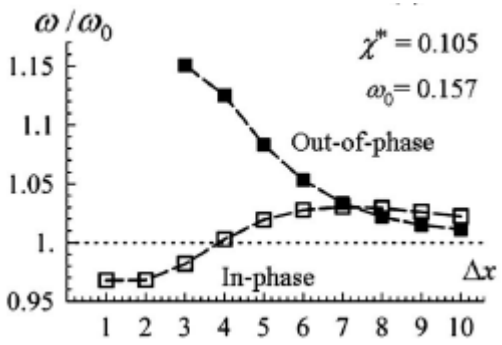
Out-of-phase Sync



No Mechanical Coupling



With Mechanical Coupling



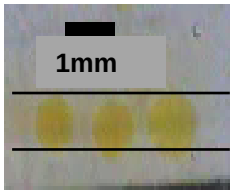
Balazs Group Simulation

Smith, Vaia et al. submitted 2012

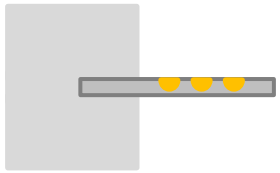
Putting Blocks Together: Three Patch Actuator

Cut actuator from patterned sheet

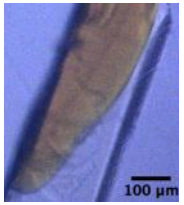
Top

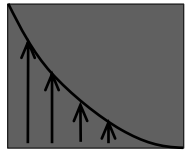


Clamp in PDMS



Gradient in Ru leads to gradient in strain upon swell-deswell

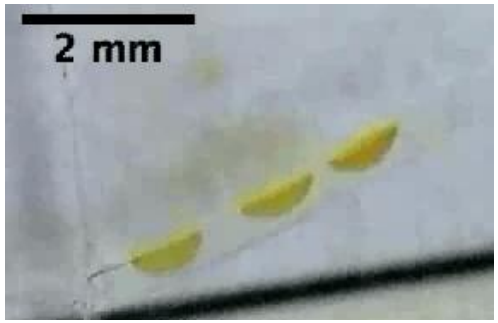




x

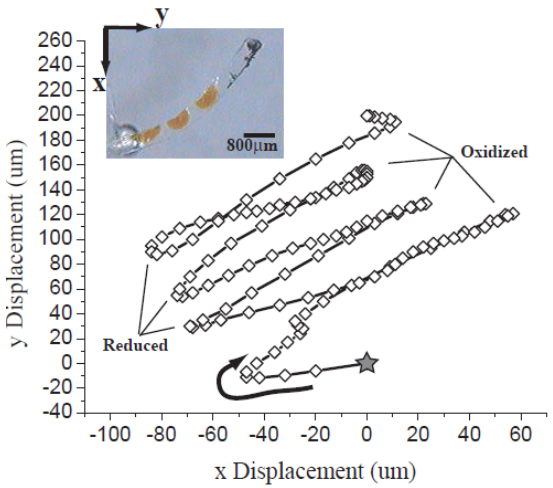
y

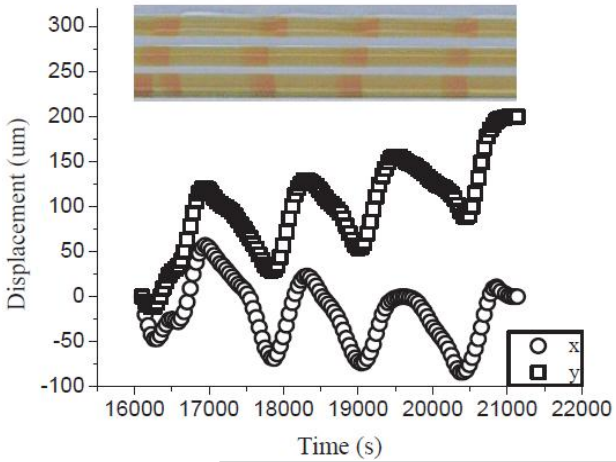
Side



5x1x0.4mm cantilever
Period: 30 min.

0.08M Sodium Bromate
0.02M Malonic Acid
0.7M Nitric Acid





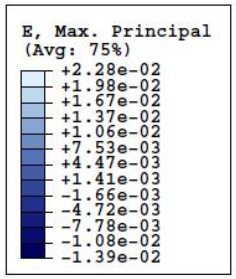
1 patch cantilever
- Amp 38.6 +/- 7.4 um
- Period = 1369 +/- 107um

3 patch cantilever
- Amp 162 +/- 36 um
- Period = 1587 +/- 410um

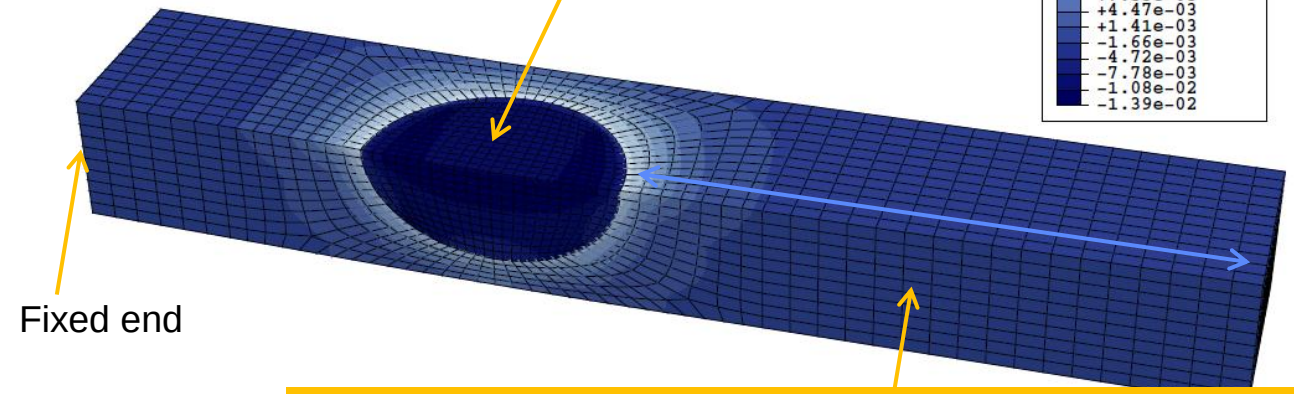
Pattern design and mechanics leads to cooperative swell-deswell with motion amplification of 15x over cube

FEA Modeling

Apply temp locally to impart
1.5% strain in patch



Half of the cantilever is modeled



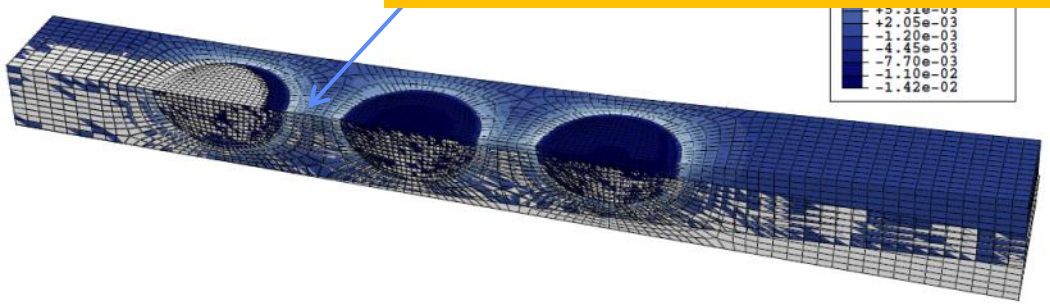
1500um

Fixed end

- Max principal strain outside patch: 2.3%
- Max principal strain drops to zero beyond ~300um, <0.5% after 200um
  - Within these distances we expect mechanical effects on coupling

- 1 patch tip displacement = 42um
- 3 patch tip displacement = 191um

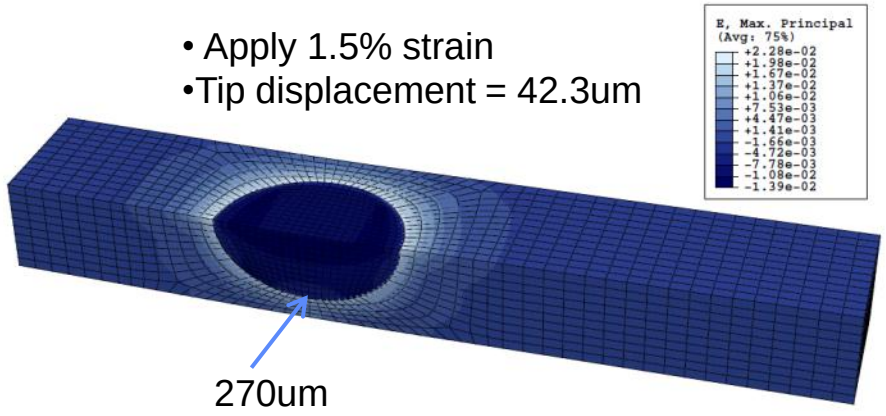
Experimental = 38.6um
Experimental = 162um



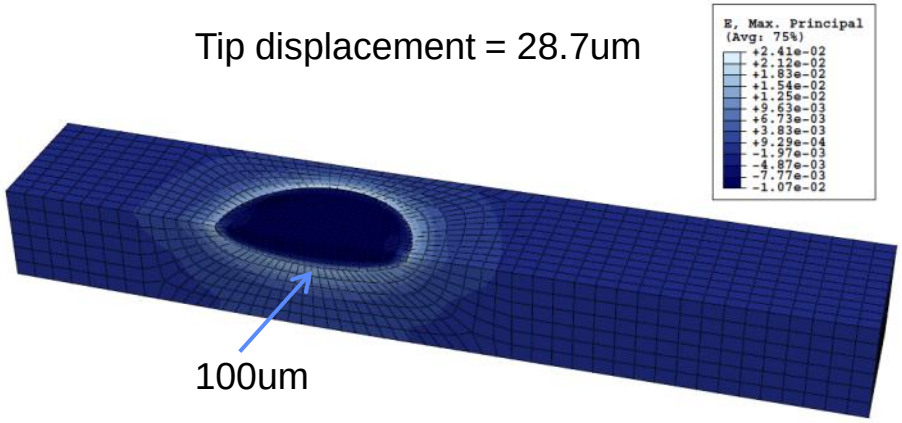
Smith, Vaia et al. submitted 2012

FEA: Optimal Stain Generator Profile

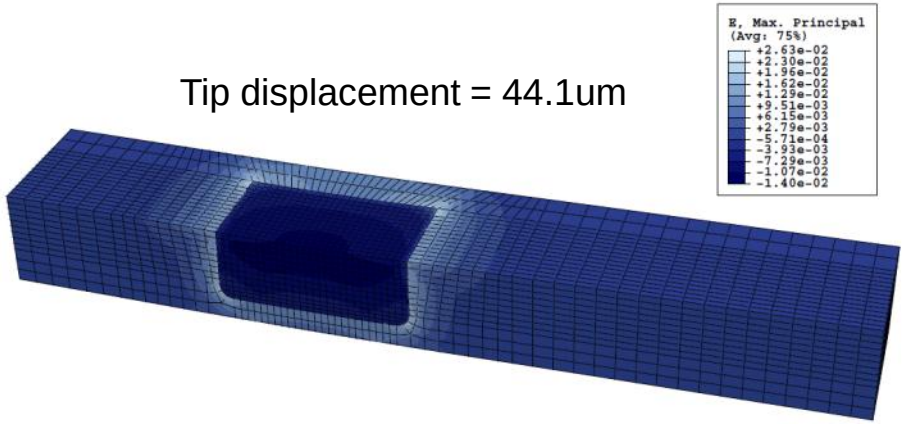
- Apply 1.5% strain
- Tip displacement = 42.3um



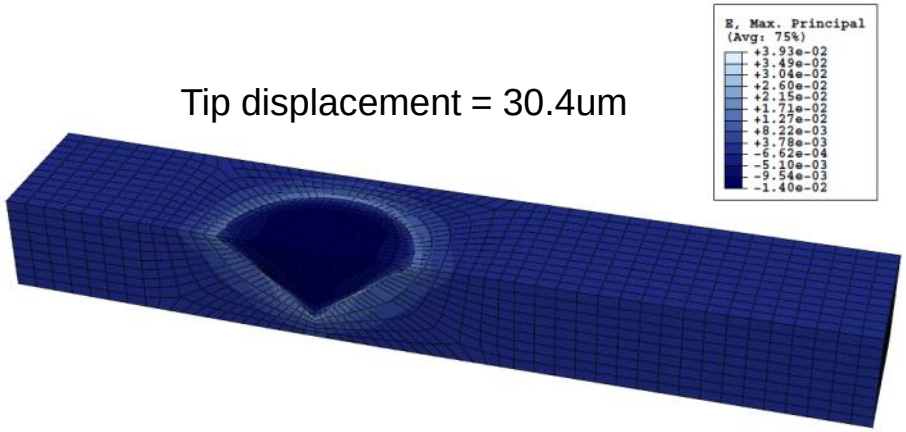
Tip displacement = 28.7um



Tip displacement = 44.1um



Tip displacement = 30.4um

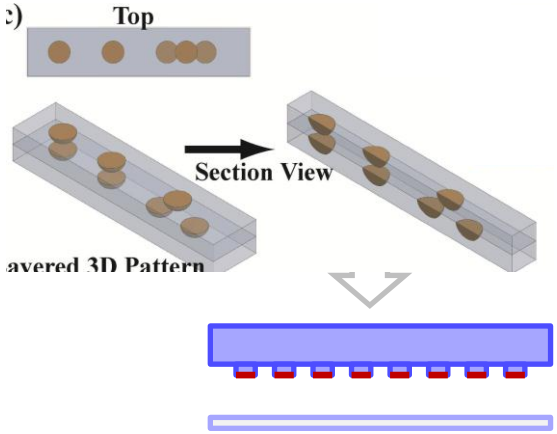


Which shapes give greatest degree deflections?
Which shapes lead to greatest coupling through strain?
How do varying material properties affect behavior?

Smith, Vaia et al. submitted 2012

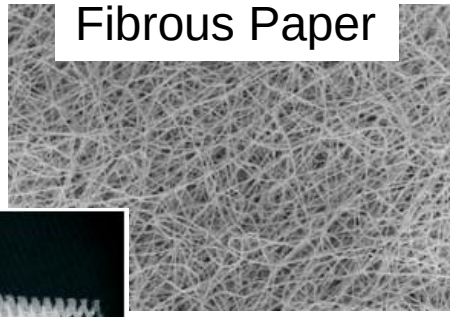
Next Step: Heterogeneous Autonomic Gels

Patterning: Additive Mfg, 2D Stamping, 3D microtrusses, 3D BZ colloid mixtures

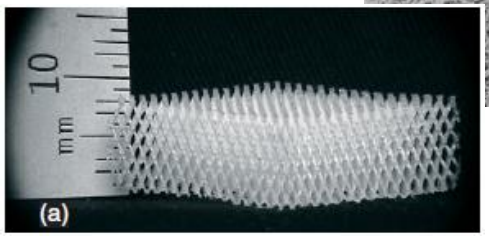


Puopolo, Vaidyanathan OSU

Fibrous Paper

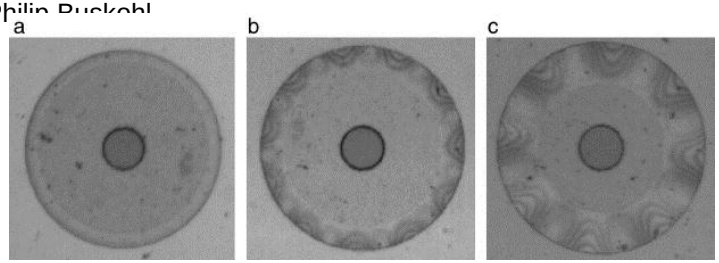


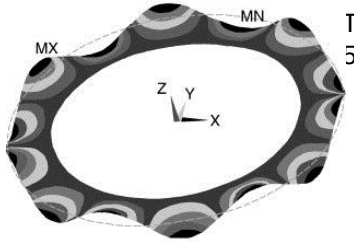
Jacobsen et al. *Adv. Mater.* **19** 2007



Mechanical Design: Bi- / meta- stability for speed; wave interference

Philip Ruskohl

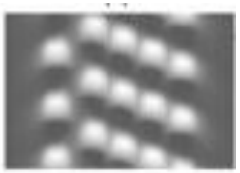


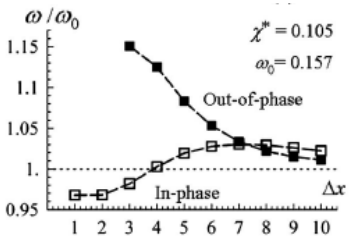


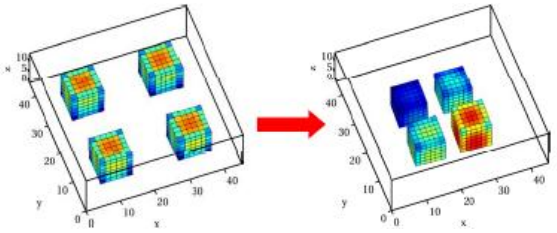
Thin Film Solids, 516, 2008, 4070

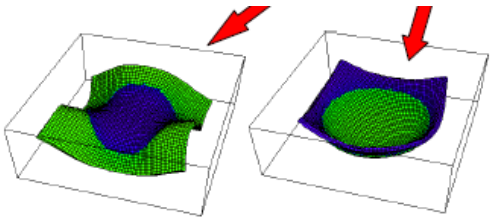
Model Validation: crosslink network, transduction, material properties

Balazs et al.

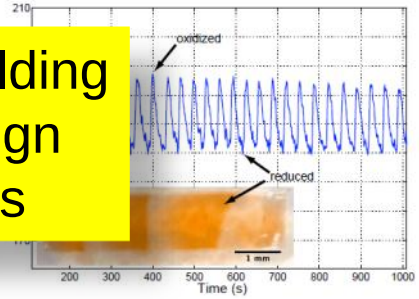
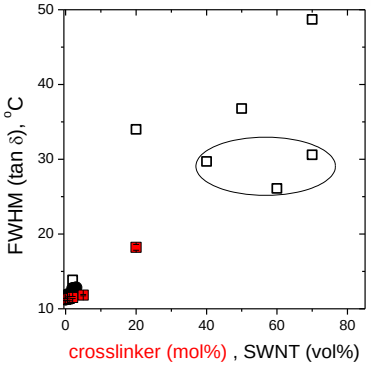
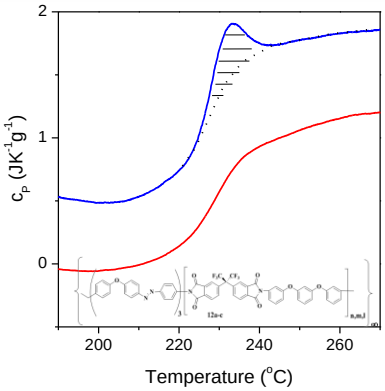
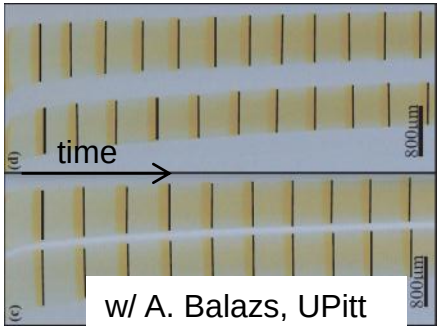
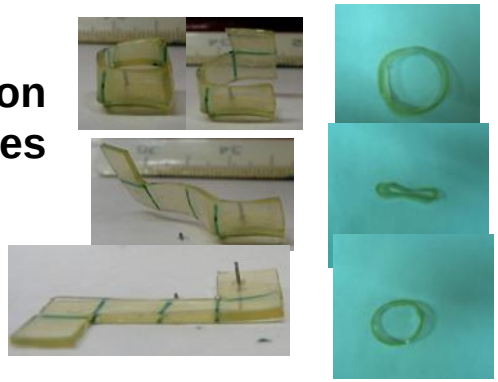
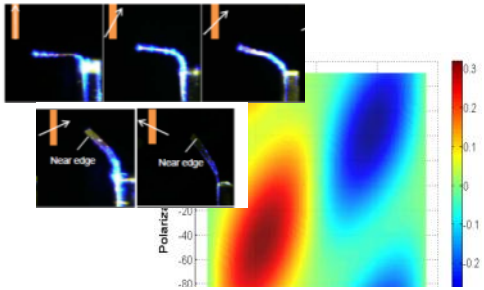
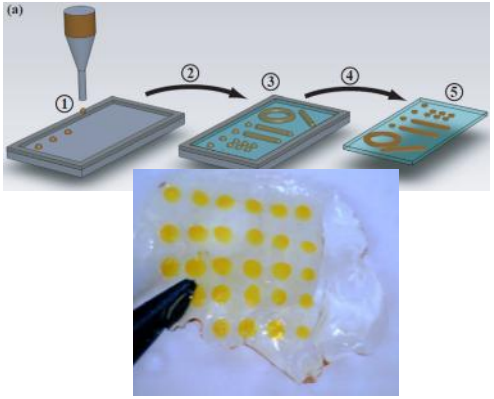








Program Status

	HT Thermal Shape Memory	PhotoChem-Mechanical	Autonomic Chemo-Mechanical
Building Blocks	 w/ L-S Tan, AFRL	 w/ T. White & L-S Tan, AFRL	
Predictive Models			 w/ A. Balazs, UPitt M. Smith, Hope C.
Fabrication of Devices		 w/T. White & M. Smith, Hope C.	

Goal: Develop responsive material building blocks & fabrication to establish design tools for functional material systems